A new theory for the anisotropic etching of silicon and some underdeveloped chemical micromachining concepts

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A new model for the anisotropic etching of Si predicts a maximum dissolution rate at 22 wt. % $KOH:H_2O$ and a zero etch rate at the solubility limit of KOH in H_2O, which is in good agreement with experiments on {100} and {110} Si. However, the {111} etch rate may decrease continuously with OH^- concentration (no peak) and appears to be blocked by $OH:3H_2O$ or some other threefold complexes that attach themselves to every bond on this surface. The strong effects of organics on the etching of convex corners, groove bottoms, and the relative etch rates on the three major orientations are noted, as are the possible effects of Fe and other impurities on the etching velocity and geometry of misorientation steps. The ability to pass current preferentially down the face of these steps needs to be developed before several unique functions can be tested. These include the fabrication of atomic wires, chiral molecule filters, and a sort of flying carpet type of air foil; the functions of which are based on clockwise facing steps on all four walls of holes in single crystal wafers. Vertical thin studs containing controlled pore diameters ranging from 1 to 1000 nm can be formed easily into semipermeable membranes and other complex structures. These interdigitated three dimensional structures can be applied to desalinization, fuel cells, biological membrane and neuron simulation, chemical and nuclear reaction schemes, and much more. The fabrication of micromirrors and lenses is also discussed.

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I. INTRODUCTION

The fields of anisotropic chemical etching and micromachining have grown rapidly in the last decade, as witness a recent international conference where 340 papers were presented. A large fraction of these were based on Si micromachining.[1] However, we have been inhibited from attempting some of the potentially more highly leveraged applications by the lack of understanding of the etch mechanisms and how to intelligently modify the gross or localized atomic structural aspects.

This paper will focus on the anisotropic etching mechanism, and how this mechanism might relate to new functions and structures, with an emphasis on those aspects that need more attention before semiconductor micromachining can enter the ranks as a distinct and important entity in science and technology. I will emphasize efforts at the University of New Mexico in the Center for High Technology Materials, along with theoretical work of our colleagues E. D. Palik and O. J. Glembocki at the Naval Research Laboratory. The excellent work on micromotors and sensors of many types is well covered in Ref. 1.

II. ANISOTROPIC ETCH MECHANISMS

There have been very few studies dedicated to understanding why the etch rates are so incredibly different on the different crystal planes of Si, the rates being about 200 times larger on the (100) and 400 times larger on the (110) than on the (111) surfaces in KOH:water solutions.[2,3] We have not been able to improve these ratios over the last 16 years, although we have learned to make them *smaller* when we could afford to and when we wanted much less convex corner etching.[4] We also do not know why the etch rate and

surface quality on the (100) surface are so variable when using $KOH:H_2O$ mixtures. From experiments by the author in Puebla, Mexico, we also know that the addition of 200 ppm of $FeCl_3$ to 45 wt. % $KOH:H_2O$ doubles the etch rate on (110) Si at 40 °C. However, we do not know the effect of $FeCl_3$ on the etching of the (111) surfaces or on convex corners.

An extensive early study attempted to infer something about the mechanism of KOH:water by adding isopropyl alcohol to the mixture,[5] but no definitive suggestions were made to explain the large differences in etch rates other than general observations regarding the dangling bond densities on different orientations. These are 1.36×10^{15}, 0.96×10^{15}, and 0.78×10^{15} cm^{-2} on the (100):(110):(111), respectively, which are not in the proper sequence nor do they have the proper relative values to explain the 200:400:1 etch rate ratios mentioned earlier for these crystal surfaces.

A so-called working hypothesis[6] for the slow etch rate on the (111) suggested that the etching of Si in $KOH:H_2O$ occurred by a simultaneous oxidation and dissolution process similar to that proposed for the etching of Si in mixtures of HNO_3 and HF acids.[7] This was reasonable on the basis that the etch rate of the (111) surface of Si was of the same magnitude as it was for thermally grown SiO_2, at least in the temperature range of 85 °C. On this idea, the (111) was thought to develop an oxide in the solution that blocked the etching. Thus the subsequent oxide dissolution became the limiting step in the Si etching process on the (111) surface. The other crystal planes were thought to oxidize more slowly in the solution and not to have a chance to fully passivate themselves, so they dissolved continuously. However, on this model the etch rate of the (111) at lower temperatures,

say 25 °C, should have been as slow as that for SiO₂. It was not. The (111) rate was at least three times higher. Furthermore, it has now been shown that the (111) need not be the most rapidly oxidizing plane, as thought earlier.[8] In fact, in some circumstances, the (110) may be the first to oxidize,[9] again throwing the simple "working hypothesis" into question.

A recent model is considerably more promising. It proposes that hydration complexes of the K⁺ and OH⁻ are a dominant factor and that the (111) is blocked from the etching process by an inactive complex.[10,11] It was first suggested that the (111) dissolution might be blocked by the solvation complex of three water molecules around an OH⁻ ion,[10] reminiscent of the hydronium ion complex that forms when water molecules surround the H⁺ ion in acid solutions. It is often spoken of in terms of OH:3H₂O⁻ or the H₇O₄⁻ complex.[12] These "tripod ions" with three water molecules as the legs were thought to attach to essentially every single dangling bond on the threefold symmetric (111) surface, thereby greatly inhibiting the dissolution process. It was also proposed that the etch rate of the other planes should drop to zero when the solution was saturated with KOH. Dropping a Si wafer in such a saturated solution was said to be something like dropping a KOH pellet into a saturated KOH solution. The pellet would drop to the bottom of the beaker without dissolving since the water molecules were all solvated and there were no free water molecules to dissolve the pellet. The same thing should happen to a Si "pellet" if the free water molecules were required to dissolve the Si. Poetic!

The above extremely simple model was only qualitative until Glembocki and Palik analyzed the data of de Guel and Kendall on several hydroxides,[11] namely, KOH, NaOH, and LiOH. This analysis has supported the model in all of its main features. In addition, the detailed treatment suggests the possibility that the (111) may dissolve quite differently from the other crystal planes. In fact, it appears that the OH⁻ ion is not required at all for dissolving the (111), but only the free water molecules. This surprising suggestion is supported by the observation of Clark et al.,[13] that the etch rate of the (111) decreases continuously with increasing OH⁻ ion concentration. As a consequence, the etch ratios between the fast etching planes and the (111) should increase continuously with KOH concentration. Such an increase in etch ratio had already been reported,[3] but its possible significance was not appreciated until the data of Clark et al. and the detailed theory came along.

The model[11] starts by choosing a reasonable chemical reaction for the dissolution of Si in KOH or other hydroxide. It then uses literature values of the chemical activity of water in KOH to obtain the mean hydration numbers for the K⁺ and OH⁻ ions in KOH, or the equivalent values for the other hydroxides. The relative dissolution rate is then predicted for each hydroxide by assuming a two-step reaction involving free water molecules and OH⁻ ions as had previously been proposed by Palik, et al.[14] in their studies of electrolytic etching in KOH:H₂O. The reaction rate R was given by

$$R = C \, (H_2O)^r \, (OH^-)^s, \qquad (1)$$

where r and s are the number of free H₂O and OH⁻ species

required for the dissolution process, and C is a prefactor that includes the constant concentration of the Si surface, as well as the activation energy of the reaction.

For KOH, the above model predicts a distinct maximum in the etch rate at 22 wt. % for r and s both chosen as 2. The data of Fig. 1(a) are in quite good agreement with such a simple model. Thus, the overall chemical reaction that gives the best fit to the data is the following:

$$Si + 2H_2O + 2OH^- \rightarrow Si(OH)_2(O^-)_2 + 2H_2, \qquad (2)$$

where it is noted that the reaction rate R depends primarily on the reactants on the left side. The products may be somewhat different from those shown (e.g., other silicates), although the release of two H₂ molecules for each dissolved Si atom was indeed confirmed experimentally.[14] The mean hydration number n_H is 5 at low KOH concentration and then decreases to about 3 at 50 wt. %, as shown in Fig. 1(b). These variable values of n_H come directly from analysis of the chemical activity in the literature. The n_H values enter in a modified version of Eq. (1) above that accounts for the free (unhydrated) H₂O molecules rather than the total H₂O. Incidentally, the decrease of n_H to about 3 that is shown in Fig. 1(b) relates to the hydration number in the bulk of the solution and does not say anything directly about the adsorption of the tripod complex on the {111} surface. This latter possibility was inferred from the extremely slow etching kinetics on the {111}.

The prediction of the peak etch rate is quite good, as is the overall shape of the curve. The etch rate at very high KOH concentrations is indeed small (and rather variable), but it does not actually go to zero as predicted. This may be due to fluctuations in the free and bound states of water, leaving
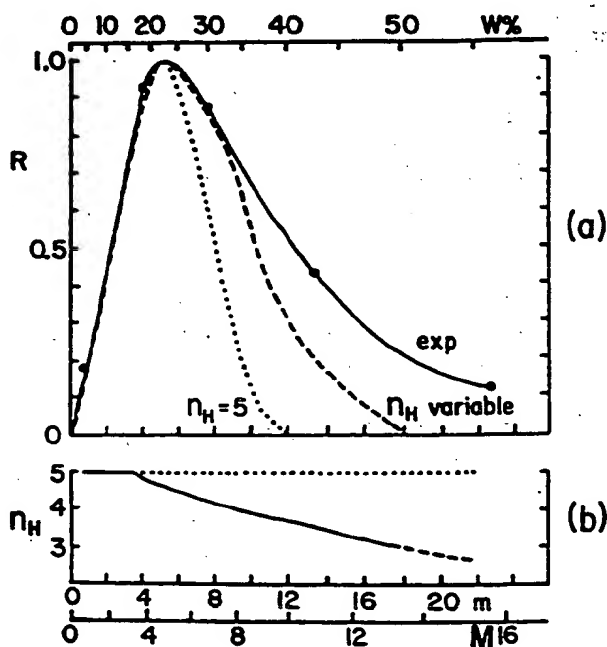

FIG. 1. (a) Normalized etch rates for KOH:H₂O on (100) Si at 30 °C; experimental data and two calculated fits based on a mean hydration number of 5 and on one varying as in (b) based on chemical activity analysis.

some water momentarily free to participate in etching. The apparent excess etching at high KOH concentrations shown in Fig. 1(a) may also be due to the presence of crystal defects in the Si or trace quantities of heavy metals such as iron. This difference between theory and experiment raises important fundamental questions. It should be pointed out that stirring of the solution is probably not a factor at these high concentrations, although it can have a measurable effect on the position of the peak at lower concentrations.[3,11]

Similar qualitative agreement is seen for the occurrence of a peak etch rate for both NaOH and CsOH,[11] with the data for CsOH on Si coming from Clark, et al.[13] On the other hand, it predicts a monotonic *increase* in etch rate on the (110) and (100) with LiOH concentration (without a peak) because of the low mean hydration number in this system. (This is the opposite behavior to that on the (111) mentioned earlier). The etch rate data for LiOH are too sparse and variable to make a definite statement, but the maximum or peak is indeed not apparent in the preliminary data,[11] at least up to saturation at 5 M.

For completeness, it should be noted that very recent data[15] on NH$_4$OH:H$_2$O etching of (100) Si also shows a peak etch rate on the (100) at about 9 wt. %, but this system has not been treated theoretically. The etch rate at the peak in NH$_4$OH at 75 °C is only about 50% of that of KOH at its peak at the same temperature. It was also noted that the etched (100) surfaces have large numbers of pyramidal hillocks. The best reported etch ratio is only about 25:1 for the (100):(111). However, a possible advantage is the much lower heavy metal concentrations available in reagent grades of this chemical as compared to the group I hydroxides[15].

Before leaving the topic of mechanisms, I should point out what happens when organics are added to KOH:H$_2$O. The etch rate ratios on the three major planes change considerably,[3] and the corner etching of convex corners becomes much less severe.[4] The same kind of changes occur when etching is done in solutions of ethylene-diamine:pyrocatechol:water, which is called either EDP or EPW in the literature. If we speak in round numbers, typical etch ratios in either the isopropyl[5] alcohol:KOH:H$_2$O or solutions containing ethylenediamine[16,17] are 200:100:10 for the (100):(110):(111), respectively. These ratios should be compared to those in KOH:H$_2$O of 200:400:1 for these same three surfaces, as mentioned earlier. The etch rates of many other crystal planes in both the KOH and ethylenediamine (EDA) systems are reported in the papers on the Wagon Wheel Method and the review of Kaminsky.[18]

If one studies the above etch ratios, it is found that the organics don't affect the (100) very much, but they slow down the (110) rate by a factor of 4 and speed up the rate n the (111) by a factor of 10. Strong medicine indeed! On the basis of the complexing model discussed earlier, one can speculate that the organic molecules somehow disrupt the passivation process on the (111), perhaps by competing with the "OH:3H$_2$O tripods" for the threefold sites. The organics may also attach themselves to the twofold symmetric sites on the (110), thereby sl wing down the etch rate on this surface. The (100) is the least affected surface, perhaps be-

cause the tripods don't attach very well to the double bonds on the fourfold surface in KOH and the organics don't change the situation too much. It sh uld be pointed out that the ethylenediamine, as well as the hydrazine, mixtures both have high OH$^-$ concentrations due to each of these m lecules grabbing an H$^+$ off of HOH molecules, thereby releasing OH$^-$ ions. Water must be added to both of these solutions in order to dissolve Si. Experimental peaks in the etch rates also occur in these mixtures.[16,17]

III. STEPS, KINKS, AND IMPURITIES

In the initial model to explain the linear dependence of etch rate on the misorientation of the groove from the perfect {111} alignment, steps on the {111} sidewalls of the slightly misaligned narrow grooves were a prominent feature of the process.[2,6] The steps on facing walls of a narrow groove faced in opposite directions and were shown by time lapse photographs to move in opposite directions during the dissolution process.[2] This basic model is shown in Fig. 2. The angle β that the step makes with the top of the groove is 112° t 120°. Another set of steps with an angle β' of about 60° is seen less often, but the primary β-type steps often change abruptly to β'-type steps, as shown in Fig. 3. There are also occasional regions of steps marked D in Fig. 3 that subtend 90° to the top edge of the original groove.

The dark field optical photos shown in Fig. 3 illustrate several important aspects of the process. They show the steps on the walls of a deep groove at two stages in the KOH etching process, the first after a brief 10 min etch at 23 °C in 42 wt% KOH:H$_2$O of a previously etched sample that was stored in the lab for several months. The sample had originally been etched in the same solution in narrow 60 μm wide vertical grooves and equivalent width studs all the way through a (110) Si wafer of 350 μm thickness, stopping at a thick oxide on the back of the slice. Before attempting the two-step procedure in KOH:H$_2$O, the thin studs were treated in standard acid cleanups which removed the oxide masks. A white residue is seen in the top photo after the first 10 min re-etch in KOH at 23 °C. The second phot is after 5 additional h under the same conditions. The third is a composite of both photos, with the contrast of the second phot
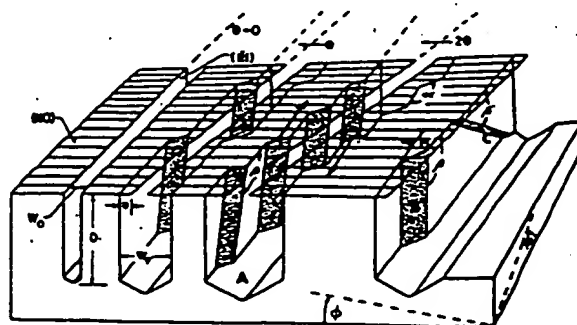

FIG. 2. Model showing the effect of oxide mask misorientation θ from the (110):(1$\bar{1}$1) intersection. (Drawing adapted from Refs. 2 and 6.)

FIG. 3. Optical photos showing leftward movement of steps on a {111} plane during KOH:H₂O etching of Si. See the text.

reversed (black steps). It shows a leftward motion of about 12 μm of all the steps.

There is not much dependence of the step etching velocity on the angle of the steps, or on the step height. Steps of a few atoms height are also visible at higher magnification in the Nomarski microscope. These isolated steps of atomic (or biatomic) thickness on the {111} plane generally etch somewhat faster than similarly oriented large steps. This is because they are less diffusion limited, being surrounded by a large volume of nonetching reactants on the {111}. Thus they tend to move faster and bunch into the larger steps.

The misorientation etching steps are interesting in several regards:

(1) They face in opposite directions on facing walls.[2]

(2) The steps tend to form along certain crystal directions

in a given chemical etching formulation, at least in dislocation free regions.

(3) The *faces* of the larger steps are measured at high magnification to subtend about 135° with the {111} groove walls. This appears to be some rather high index plane near the {137} family. Such large step faces are so full of peaks and valleys that it is only the tops of the peaks that define something like a plane.

(4) The facet A at the base of the wider grooves is in the {113} family. It can be quite smooth when high concentrations of KOH:H₂O are used. This facet can be suppressed and flat 90° intersecting bottoms can be obtained on vertical grooves in (110) wafers by adding a few percent of certain wetting agents like triethanolamine to the KOH:H₂O solutions.[19]

With regard to items 2 and 3 above, the effects of various impurities and organic additives on the properties of the steps have not been studied. The strong effect of a small amount of isopropyl alcohol in the KOH:H₂O mixtures was noted earlier, both on convex corners and on the etch ratios. Similar effects were noted when the etching was undertaken in solutions based on ethylenediamine, EDA. The geometry of the steps should change in some systematic fashion with the addition of these, as well as other organics. To correlate these step changes with the etch rates on the major crystal planes would be of value in devising an intelligent control of overall morphology for micromachining, as well as for better GaAs growth on Si.[20]

Significant changes in the steps would also be expected in the presence of controlled additions of Fe, especially in view of the large increase in etch rate mentioned earlier with the addition of FeCl₃. We have measured several ppm of Fe in 45 wt. % KOH solutions made from commercially available KOH pellets. Other ions would also be of interest, as would the effect of variable amounts of the inevitable dissolved CO_2 in the solutions.

These comments on the effect of impurities hark back to experiments performed by Gilman *et al.* in 1958 on the etching of LiF in Fe contaminated distilled water.[21] They found that the addition of only 2 ppm of FeF_3 to distilled water was sufficient to change the form of dislocation etch pits on LiF crystals from an indistinct 40 μm diameter to a very distinct 10 μm pyramidal pit. This striking result was attributed to Fe^{3+} ions collecting preferentially at kinks within steps. The Fe^{3+} was most effective when added as FeF_3, but was also effective when added in significantly larger quantities as $FeCl_3$, $FeBr_3$, and $Fe(NO_3)_3$. They also showed that Al^{3+} added as AlF_3 was quite effective for delineating dislocations. In this regard, it is interesting to note the strong quenching effect of a small amount of dissolved Si in NH_4OH on the etching of Al thin films[15]. The primary lessons to be learned from the work of Gilman *et al.* are in th area of methodology and the type of questions they raised. The discovery of one or more kink or step etching inhibitors (poisons) or catalysts for Si w uld be of significant value.

Another area that needs effort is the smoothing of surfaces having large steps into surfaces that consist primarily of steps of monolayer or bilayer thicknesses. In this regard, the effect of electrolytic etching in KOH:H₂O on the step prop-

erties would also be of interest,[14] as would the application of electrolytic polishing in HF:H₂O mixtures.[12]

IV. ACTIVE STEPS, CHIRAL BOXES, AND FLYING CARPETS

A technology that would be of fundamental importance would be the discovery of a method to pass current preferentially down these steps, either the large ones, or the single or double layer variety. The idea here is to develop some diffusion, or oxidation, or directional evaporation, or implantation, or electroplating, or impurity segregation, or other technology that would allow the steps (or their immediate surroundings) to preferentially carry current, with much less current being conducted on the large flat terraces between neighboring steps. Such a development would be one more way to produce "quantum or atomic wires," especially if the process could be developed and applied to monoatomic or biatomic steps.

The development of the current carrying step above might also allow an experimental evaluation of the "flying carpet" proposal. That speculative concept involved the generation of so-called microtornados inside specially micromachined holes in Si or other materials.[3] In that proposal, the air molecules were preferentially deflected at the steps [say counterclockwise (ccw) facing] on the four walls of a square funnel shaped hole. These closely spaced holes would be slightly misoriented from the orthogonal directions of the crystal so that the walls would have many ccw facing steps similar to the steps of Fig. 2. The holes would be produced all the way through a thin wafer. The steps would then be heated locally by pulsing current down the steps of each wall sequentially, thereby moving the air near the wall laterally and building up a vortex of circulating air inside each hole. The pulses down the steps on each wall would be separated by about 0.2 μs. This is the time required for an air molecule to move from one wall to another, a distance of the order of 100 μm in a typical funnel shaped hole. (The holes at the bottom of the funnels need not be very small since it is the stepped walls that are imparting the action to the molecules). Very short intense current pulses would be preferred since the heat would then be more localized to the region of the steps. The molecular reflections from the flat portions of the walls will tend to randomize the distribution and to dilute the effect. These regions can be kept cooler by not passing current across the terraces. Another approach to generating such a circulating vortex is to use pulses of high intensity light that is preferentially absorbed in the region of the steps.

The usual assumption of a zero velocity boundary condition for gas and liquid molecules at the walls of such holes would obviously have to be modified to account for the lateral forces generated by the directionally facing steps on the otherwise smooth walls. One of the main goals of such a scheme is to develop a significant pressure difference between the top and bottom of a wafer, thereby giving it aerodynamic lift, or a flying carpet effect. For example, the rotating vortices formed in the holes mentioned earlier might be electrically activated to give a compensating thrust when a strong wind sheer is detected on the surface of an

airplane wing. (Wings having multiple holes have already been shown to reduce jet fuel consumption in experiments done by McDonnell Douglas Corporation.)

There have been other potential applications proposed[3] for the aforementioned "chiral boxes." [Their chirality consists of the directionality of the atomic steps on the walls of the hole (or box) rather than in the traditional definition in terms of the clockwise (cw) or ccw twist of molecules]. One suggestion was to enclose long chain molecules in such a chiral box and to hope that they would bounce off of the cw (or ccw) facing steps in such a way as to coil up (or uncoil) into anomalously small (or anomalously long) molecules.[3] These could be extracted on a regular basis and allowed t readjust to their normal diameters, thereby applying force t a piston or other system. This method of modifying the distribution of mean molecular radii represents a potentially useful energy storage process. The metastable distribution might also find use in chemical lasers, as well as in studies of reaction kinetics.

The use of an array of these chiral holes as a chemical filter might also be considered. A mixture of right and left handed molecules would be passed through an array f say cw stepped holes. Those molecules that had collisions with the walls might have their motional properties modified depending on their handedness, thereby resulting in at least a partial separation on a single pass. Special structural arrangements might enhance the process still further.

Before getting too taken up with all of the interesting possibilities above, I should point out that the production of square holes having the desired misaligned properties and properly facing steps is not trivial. For example, imagine that a square opening etching mask such as SiO₂ is applied by photolithography to a (100) Si wafer with the square somewhat misaligned from the typical (110) directions. One might expect the inverted pyramid pit in the Si to be etched with clearly defined misalignment steps on the walls f the hole. The hole indeed starts out with the steps on all the walls, but by the time it reaches the back of the wafer the pit has four perfectly flat facets and no steps! The resulting square hole is bigger than expected and it has rotated itself to line up with the proper (110) side alignment.[23] In spite of this difficulty, it *will* be possible to produce th desired stepped hole structure, for example, by the laser induced chemical etching of misoriented holes with a square beam. More economical methods will require some innovative processing or perhaps some novel structural arrangement.

V. SEMIPERMEABLE MEMBRANE STRUCTURE

Another interesting chemical separating method has been proposed[3] and the structure has been fabricated[24] in its simplest form. This consists of a thin vertical-stud Si membrane made with anisotropic etching followed by the introduction of micropores into the membrane using anodization in HF:H₂O (with added methanol).[25] The vertical stud membrane was produced with a single photomask and etching from one side only, which is a considerable improvement over the two sided etch suggested earlier.[6] The final structure is shown in Fig. 4. This particular stud membrane is about 10-μm thick and 80-μm high, but Ref. 3 shows one
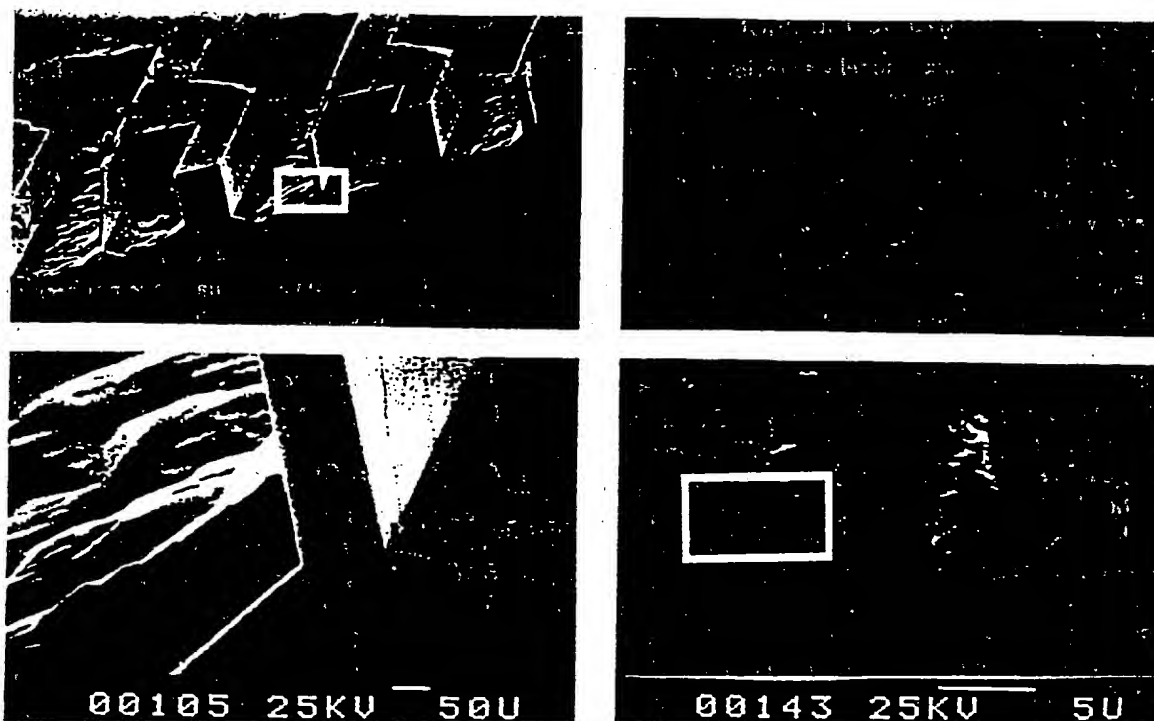
FIG. 4. Scanning electron microscopy view of vertical stud membranes and holding tanks showing 60 nm diameter pores near the base of the stud. Pores in the stud were identical.

that is only 3-μm thick and almost 300-μm high. Submicron thickness membranes are certainly possible using this technology, albeit with reduced reproducibility. The large opening at the end of the trough at A in Fig. 4 allows a voltage probe to be inserted in the liquid in the trough. The other end of the B trough is not shown, but it also has a large opening to allow a voltage probe. Additional troughs can also be constructed to perform more complex functions.

We did not succeed in passing either water or various alcohols through this porous membrane, possibly because it was either too thick or because we could not overcome the capillary forces. The pores in the 0.4 Ω cm n-type Si had diameters of about 0.06 μm. It is also quite possible that the pores did not permeate the membrane completely, stopping instead when the porous Si regions approached each other from the two sides to within a depletion layer width.[26] These problems can almost certainly be overcome. We have not yet tested it for ion transport.

The structure of Fig. 4 is shown to illustrate its ease of fabrication and to encourage new ideas based on similar interdigitated three dimensional structures. The problems of capillary forces and the hydrophobic and hydrophilic nature of th pores in Si are now being addressed for the detection of various vapors.[27] It may happen in the near future that more complex versions of the structure of Fig. 4 will be used for salt water purification, fuel cells, voltage aided ion separations, and for other separation and reaction schemes. This will require a great enlargement of our understanding of anisotropic etching, cavity sealing techniques, capillary and chemical effects in pores as small as 1 or 2 nm, protein and other pore coating schemes, as well as the physical properties of the different kinds of pores that can now be produced.[28]

VI. MIRROR AND LENS ARRAYS

The last application I will discuss is the production of arrays of reflecting mirrors on a Si wafer. This possibility resulted from an observation of optical images from spherical depressions on a (100) Si slice after the slices were thinned in a KOH:H$_2$O solution.[29] These were the result of pinholes in an oxide mask, and a wafer that was subjected to a brief KOH:H$_2$O process while the oxide still covered the wafer. This resulted in an inverted square pyramid at every pinhole.[23] After the oxide was removed and the wafer was thinned in the same KOH solution, these *square* pits became *circular* and developed into shallow nearly spherical depressions. This was an unexpected development using such a strong anisotropic etchant on a fourfold symmetric surface. Nevertheless, we can now introduce regular arrays of "purposeful pinholes" of well defined size in the etch masks by photolithography. After the thinning step, we have a regular array of spherical micromirrors with any desired f/number ranging from about $f/2$ to $f/10$. They will find application as reflectors for injection laser arrays and perhaps for geodesic lens arrays. A geodesic lens is formed from a thin film optical waveguide that is deposited on top of a spherical depression.[30] Light in the waveguide (in the plane of the film layers) can be focused in the same plane, thereby allowing various logic and other functions to be performed. There is a great deal to be learned about these depressions in Si, but they will find applications in optoelectronics, either directly or as templates on which to deposit other materials (GaAs, glass, organics) to make lens arrays and active devices.

VII. DISCUSSION AND CONCLUSIONS

A new simple physical model was reviewed to explain the striking anisotropic etching properties of Si in hydroxide solutions.[1] As the molarity of the solution increases, the OH^- concentration increases, while hydration effects steadily reduce the free H_2O concentration available for dissolution. These two effects produce a peak in the etch rate which is sensitive to the mean hydration number. The predicted behavior is in good agreement with experiments on the {100} and {110} planes. The {111} surface appears to be a special case that is strongly passivated against etching in KOH solutions by attachment of $OH:3H_2O^-$ ion complexes to each atom on this threefold symmetric surface. The unusual prediction is that only the free water molecules can attack the {111} surfaces, with no OH^- ion involvement at all. Such a situation has been reported in the water etching of powdered Si, which requires a continual shaking action to sustain the dissolution process.[31] In the case of KOH etching, it is not clear whether the proposed mechanism operates alone or is somehow part of an earlier working hypothesis involving simultaneous oxidation and dissolution of the various crystal surfaces. The apparent excess etching that occurs at high KOH concentrations may eventually give us valuable information regarding the defects present in Si. Careful etch rate experiments on Si grown under widely different growth conditions and oxygen content would be of value in this regard. It would also be interesting to apply multiple internal infrared spectroscopy[32] or other techniques to determine whether different inactive complexes could be identified on the {111} and other Si surfaces after treatment in hydroxide solutions.

The etching and geometrical properties of steps on wafers slightly misoriented from one of the major planes was also discussed. The effects of various metal and organic impurities on these steps are a valuable area of study, both for the fundamental knowledge and the likely importance of these impurities on localized and overall structure.

A technology that needs to be developed is one that allows a current to be passed along a step face without much current being conducted across the flat terraces between steps. This would allow "atomic wires" to be produced and also should allow the step regions to be heated locally. In appropriately designed arrays of chiral boxes this might result in a sort of flying carpet effect and an improved airplane wing. The multiple chiral holes might also act as a filter to partially separate left handed from right handed molecules, as well as to tighten up long chain molecules to abnormally small dimensions. However, it remains a challenge to devise an economical method of producing an array of holes having cw (or ccw) facing steps.

Thin vertical studs having controlled pore sizes over a very wide range (say 1 nm–1 μm) can be formed into voltage controllable semipermeable membranes and capillaries of various types. These interdigitated structures are easy to fabricate and it is likely they will eventually form the basis for salt water purification, fuel cells, microcapillaries, sensors of many kinds, biological membrane and neuron simulations, chemical and perhaps even nuclear microreaction vessels, etc. A great deal of new knowledge will be developed as these

become technologically viable.

Micromirror and microlens arrays can be produced using chemical etching of Si and these can be made into templates for glass, plastic, metal, and other materials. The formation of waveguide focusing elements is also possible.

So, what do we have? We have a good theory to explain how the {111} plane can dissolve 400 times slower than the {110}. Can we now go to 4000 times slower? We also have three structural concepts that have not been seriously pursued. The micromirrors will come along fine. The chiral boxes and microtornados are still in the speculative stage. The interdigitated vertical studs probably hold the richest potential for near term application.

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